Hydrogen, Fuel Cells & Infrastructure Technologies Program
2004 Annual Review
Philadelphia, Pennsylvania, May 24-27, 2004

Direct Methanol Fuel Cells

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Selected Collaborations & Commercial Interactions (C)

- **Catalyst Research & Development**

  ***Johnson Matthey:* Dr. David Thompsett** – *Pt-Ru catalysts for the anode*
  ***Superior MicroPowders:* Dr. Paolina Atanassova** – *DMFC MEAs*
  ***E-TEK / de Nora North America:* Dr. Emory de Castro** – *anode and cathode catalysis*
  ***University of Illinois:* Prof. Andrzej Wieckowski** – *basic electrocatalysis*
  ***University of New Mexico:* Prof. Plamen Atanassov** – *non-precious metal catalysis*

- **Membranes / Membrane-Electrode Assemblies**

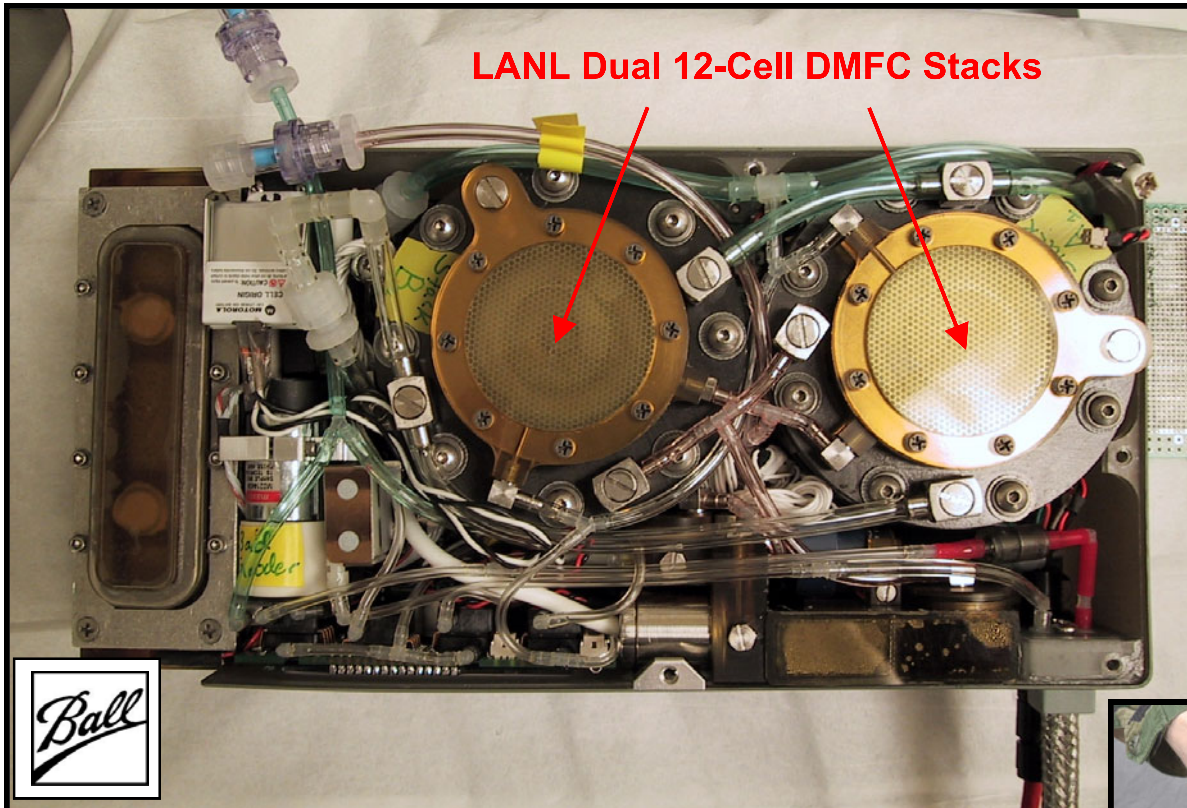
  ***Virginia Polytechnic:* Prof. James McGrath** – *alternative polymers and MEAs with significantly improved selectivity and durability*
  ***W. L. Gore:* Dr. Karine Gulati** – *membranes with improved selectivity*

- **DMFC Stacks & Sensors**

  ***Mesoscopic Devices:* Drs. Christine & Jerry Martin** – *DMFC hardware for portable applications; electrocatalysis*
  ***Ball Aerospace:* Dr. Jeff Schmidt** – *20 W portable power system for the military (DARPA Palm Power Program)*

Collaboration with Ball Aerospace (C)

Portable Power System for DARPA



Key System Specs

Rated power:	***20 W***
Voltage:	***12 V***
Specific power (72 h mission):	***500 W/kg***
Efficiency:	***33%***
Energy yield from fuel:	***2 kWh/kg***
Converter volume:	***1.6 L***
Converter weight:	***1.6 kg***

- ***LANL DMFC stacks and methanol concentration sensors integrated by Ball Aerospace into first DMFC-20 demonstration units for the military***
- ***Respectable specific power & system efficiency***

DMFC Research: Milestones & FY 2004 Funding

- **Determine the impact of Ru crossing on the oxygen reduction kinetics at the DMFC cathode.** – *March 2004*

- **Develop methods for synthesis and demonstrate new unsupported DMFC cathode catalyst with average particle size reduced by at least 40% and performance superior to the best commercial cathode catalysts.** – *March 2004*

- **Quantify losses in the active surface area of the anode and the cathode over at least 200 h of DMFC operation.** – *September 2004*

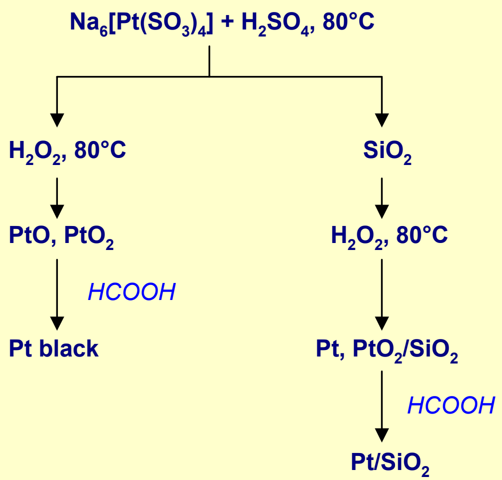
- **Total DOE Funding: $300 K**

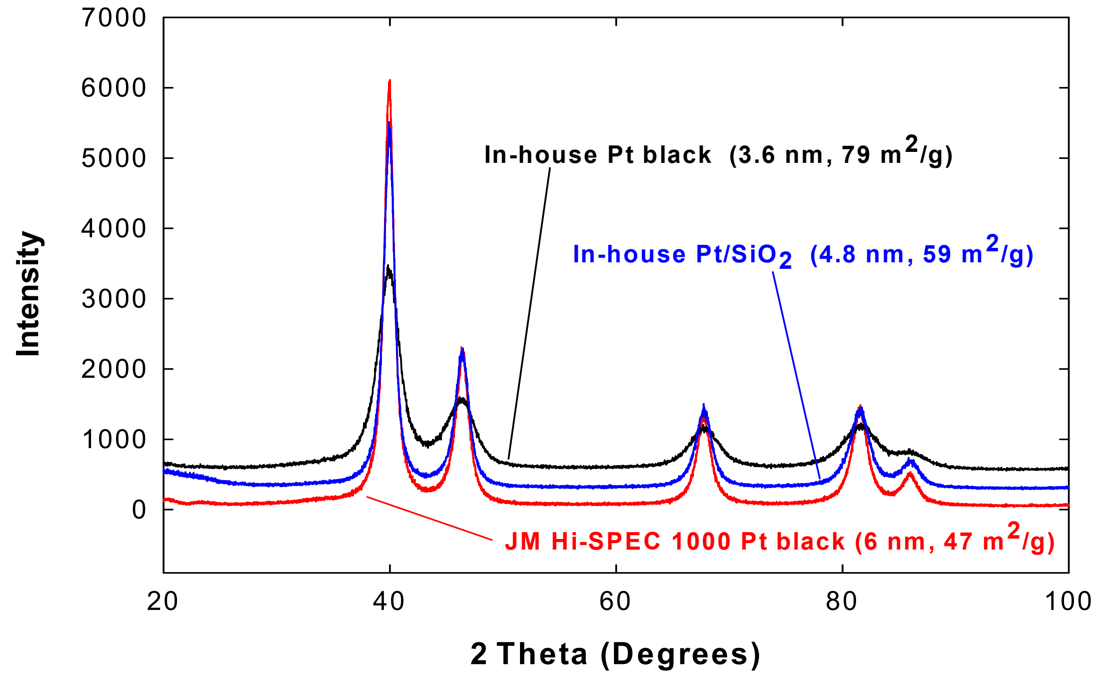
Irrespective of repeatedly high evaluation scores (3.33 in FY 2003), funding of the LANL DMFC project has been decreased in FY 2004. Reason given: *"Technology for portable power applications is near commercialization";* ***HFCIT Program, FY 2003 Merit Review and Peer Evaluation Report.***

Electrocatalysis Research

Pt Cathode Catalysts with Reduced Particle Size: Approach and XRD Patterns

Preparation of **Pt black** and **Pt/SiO_2**
Two Approaches



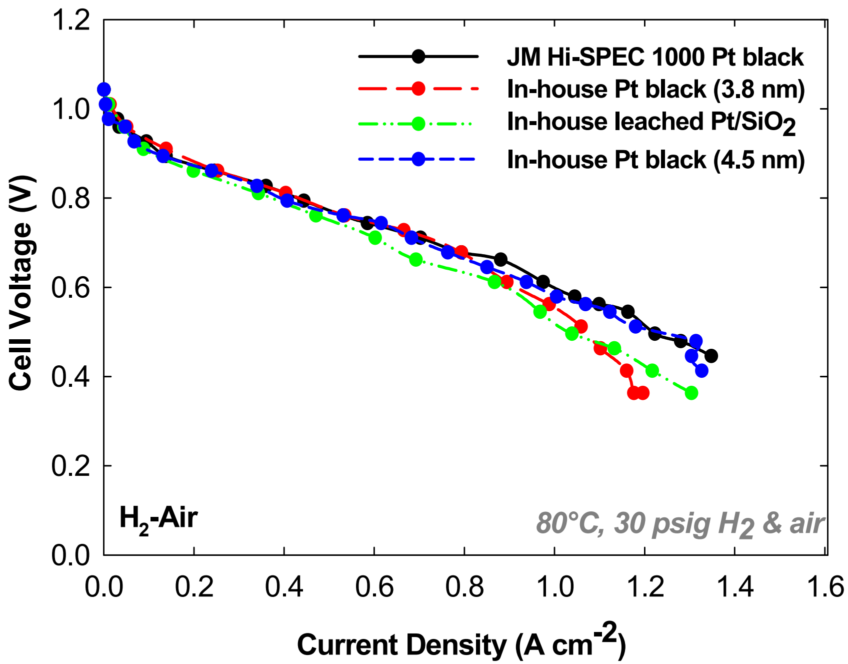


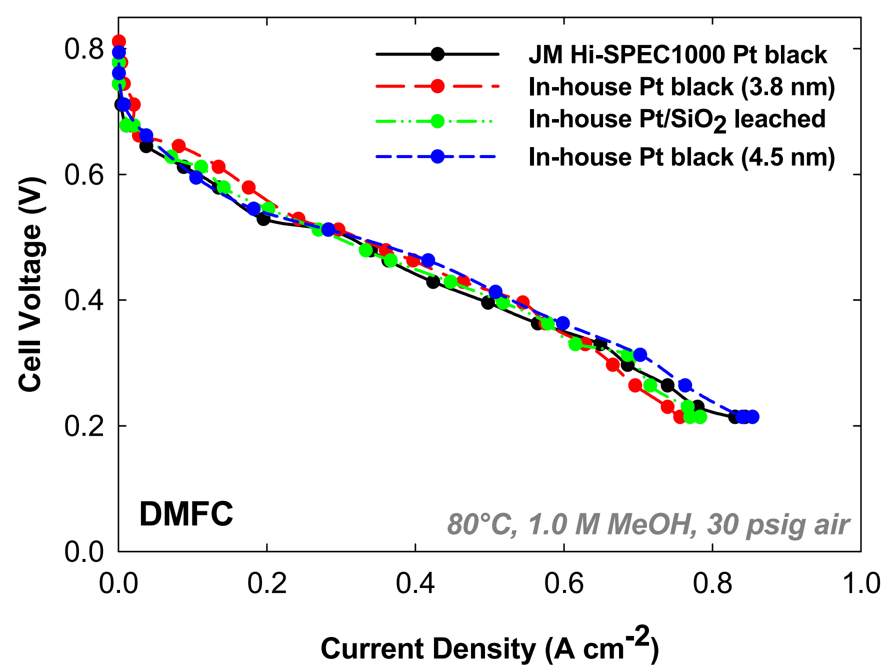
- ***Average particle size reduced from 6 nm (Johnson Matthey's HiSPEC™ 1000, the state-of-the-art Pt black catalyst for DMFCs) to 3.6 nm and 4.8 nm, for Pt black and Pt/SiO_2 catalysts, respectively.***

<u>40% higher dispersion of Pt cathode catalyst achieved (2004 Milestone)</u>

Electrocatalysis Research

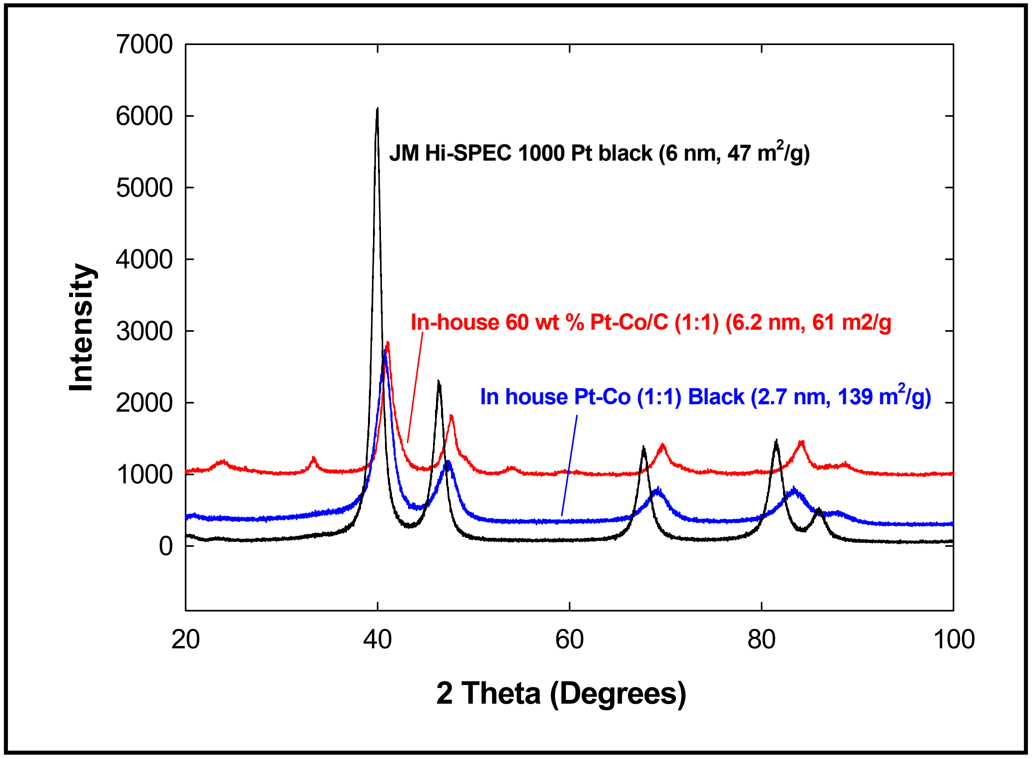
Pt Cathode Catalysts with Reduced Particle Size: Fuel Test Cell Data





- ***Performance of newly synthesized Pt catalysts matches that of the best commercial DMFC cathode catalysts.***
- ***Catalyst utilization needs to be improved in order to take full advantage of the smaller particle size of LANL's catalysts.***

Electrocatalysis Research
Pt-Co Binary Cathode Catalysts



- ***Developed two new synthesis approaches for Pt-Co binary catalysts.***
- ***High temperature method: Uniquely high metal-loading for Pt-Co/C catalyst (up to 60 wt%) and small average particle size (6.2 nm).***
- ***Low temperature method: Very small average particle size of unsupported catalyst (~ 2.7 nm – 55% particle size reduction relative to HiSPEC™ 1000).***

Membrane / MEA Research
Objectives

Alternative aromatic hydrocarbon-based membranes for fuel cells:

- ✓ *High conductivity, good mechanical properties and chemical stability*
- ✓ *Low methanol permeability*
- ✓ *At least an order of magnitude lower cost*

Ⓒ ***Collaboration with Virginia Tech***

Key technical issue:

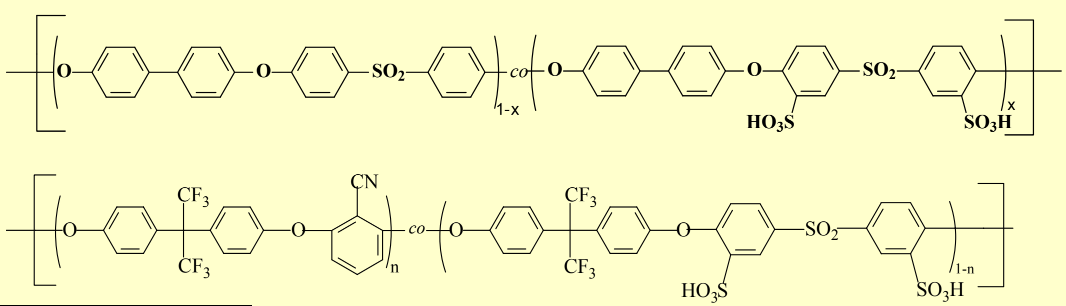
- ✓ *Performance loss due to interfacial incompatibility with Nafion-bonded electrode*

Research focus

- ✓ *Develop membranes compatible with Nafion-bonded electrodes*
- ✓ *Determine initial and long-term fuel cell performance of MEAs*

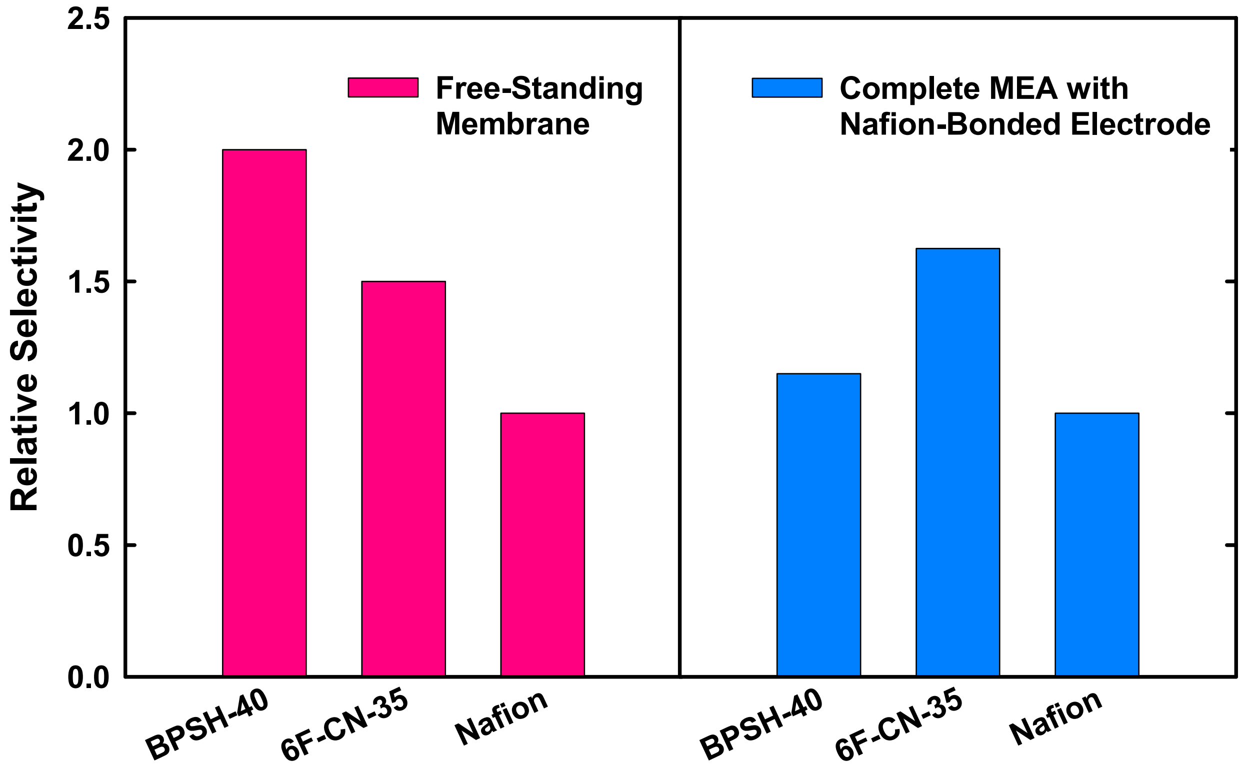
BPSH-XX

6FCN-XX



XX - *percentage of disulfonated monomer units*

Membrane / MEA Research
Membrane vs. MEA Selectivity



Membrane Selectivity

Ratio of proton conductivity to methanol permeability

MEA Selectivity

$$\alpha = \frac{1}{HFR \times \varsigma_{\lim,n}}$$

HFR = MEA impedance

ζ = limiting MeOH crossover value (at OCV)

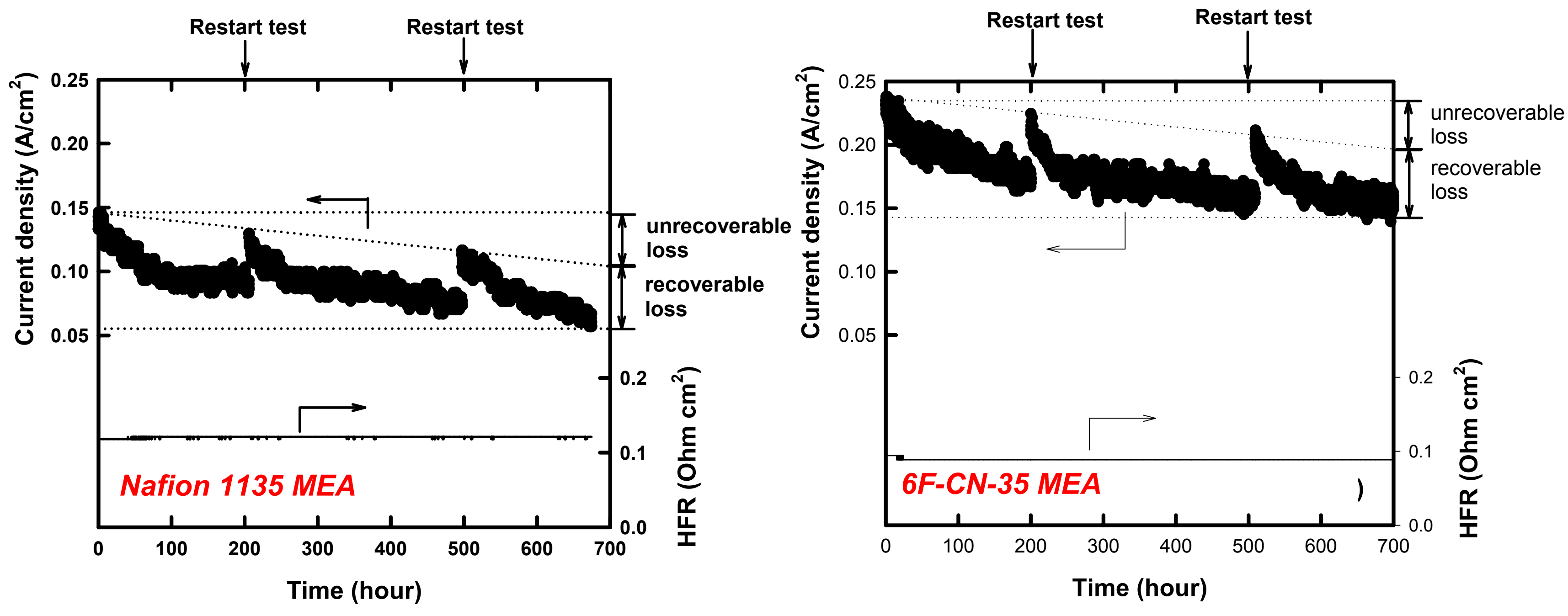
Relative Selectivity

Membrane-to-Nafion selectivity ratio

- ***Expected selectivity gains of BPSH-40 not realized in fuel cell testing.***
- ***6F-CN-35 MEA exhibits much higher selectivity than regular Nafion MEA.***

Membrane / MEA Research

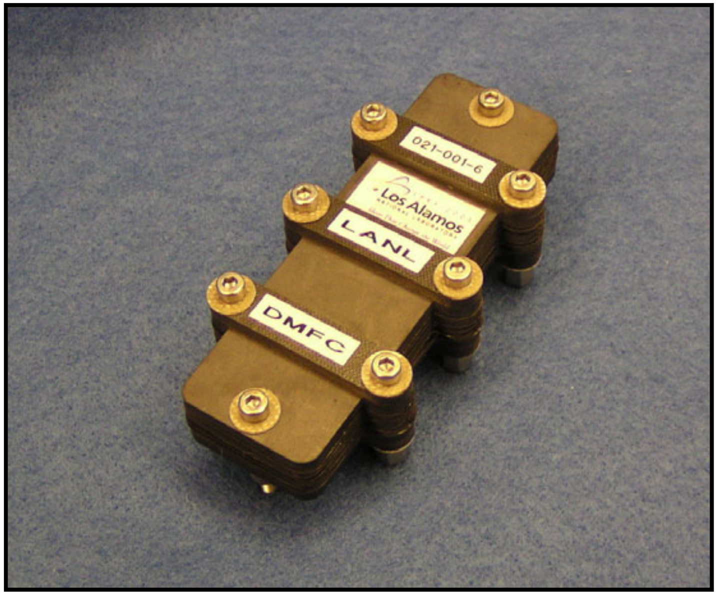
Performance Durability (80°C, 0.5 V)

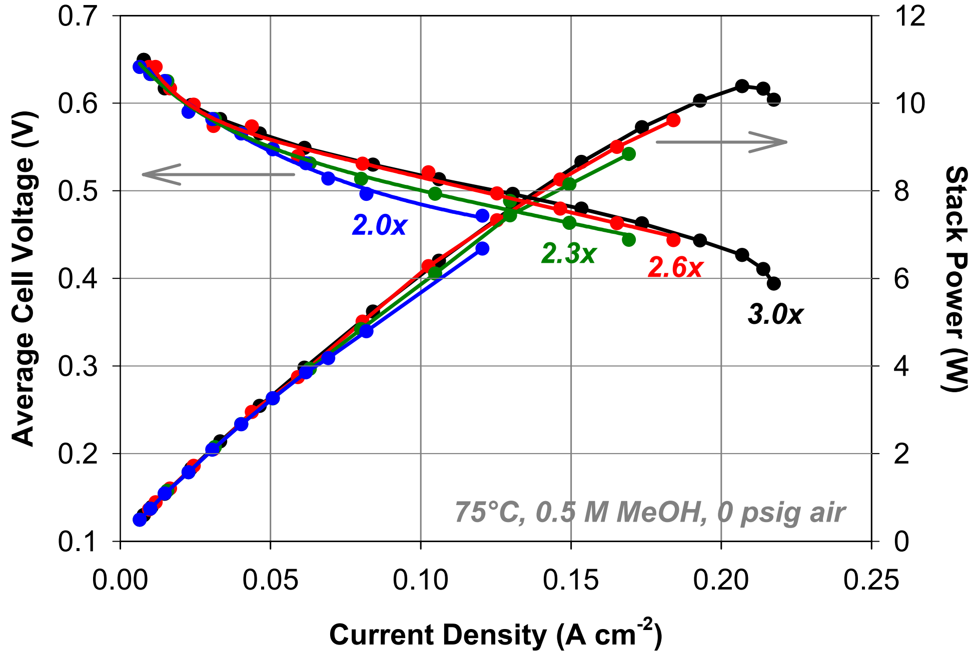


- ***Good and stable membrane/electrode interface indicated by no change in the resistance of 6F-CN-35 MEA over time.***
- ***Similar 700-hour performance losses for 6F-CN-35 and Nafion MEAs***
- ***Much higher initial performance of 6F-CN-35 maintained throughout the life test → significant achievement in the alternative DMFC membrane research.***

High Specific-Power Stack for Portable Applications

Short Six-Cell Stack Testing





First test of high specific-power stack: (i) uniform operation of individual cells, (ii) very little sensitivity to the air flow, (iii) anode-limited performance.

<u>Growing industrial interest; significant technology transfer potential</u>

High specific-power stack project currently supported by
Los Alamos National Laboratory's Technology Maturation Fund

High Specific-Power Stack for Portable Applications

Stack Performance vs. DOE Technical Targets

- ***Expected maximum specific power of the 25-cell stack: 400 - 500 W/kg.***
- ***Stack performance promises to exceed DOE's Technical Targets for Consumer Electronics systems for both 2006 & 2010***

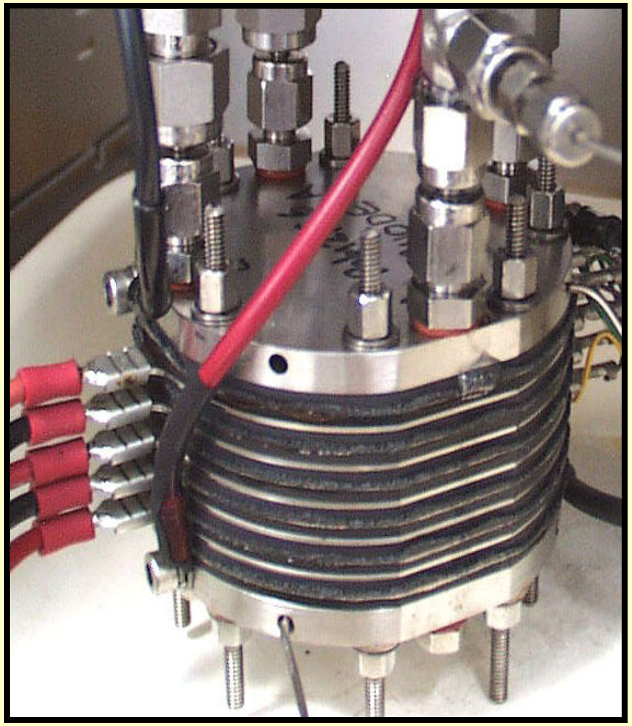
Table 3.4.7. Technical Targets: Consumer Electronics (sub-Watt to 50-Watt)[a]

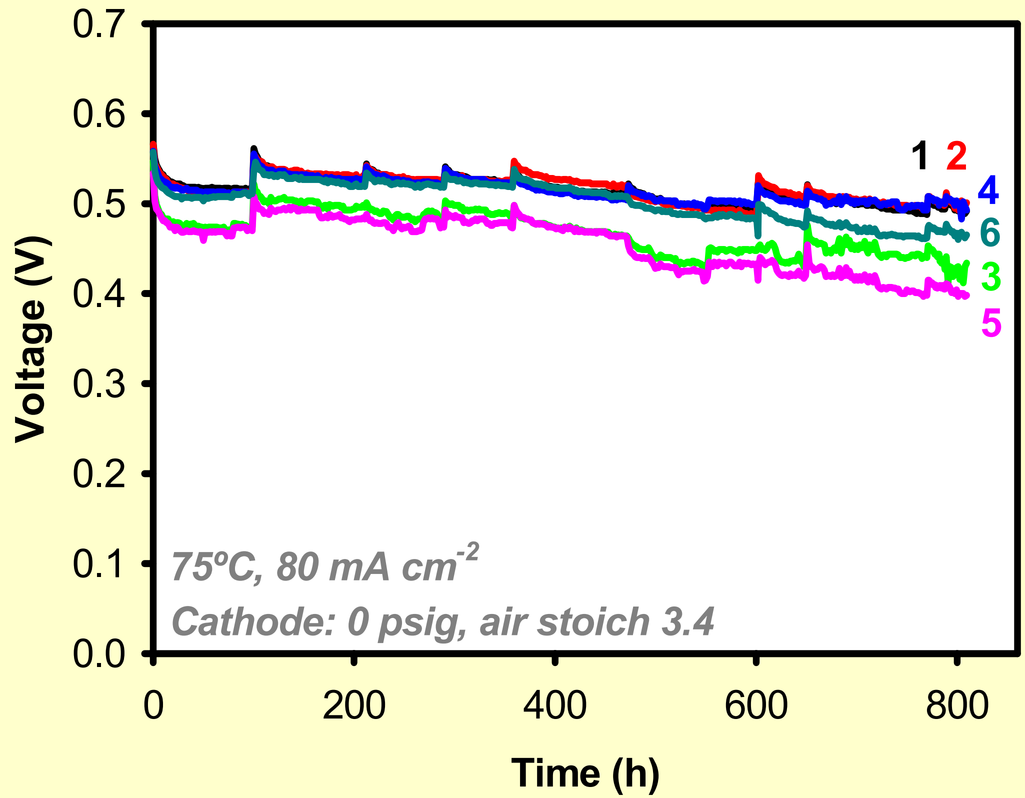
Characteristics	Units	Calendar year		
		2003 status	2006	2010
Specific Power	W/kg	unavailable	30	100
Power Density	W/L		30	100
Energy Density	W-h/L		500	1,000
Cost	$/W		5	3
Lifetime	hours		1,000	5,000

[a]Few sub-watt to 50-watt fuel cell systems exist and it is premature to specify current status.

Durability Research

850-Hour DMFC Life Test: Possible Causes of Cell Performance Loss

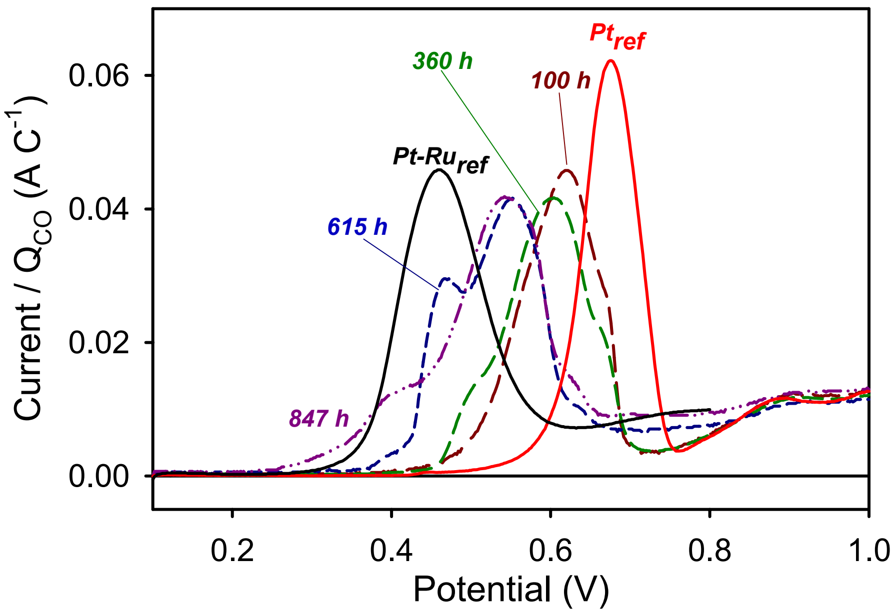


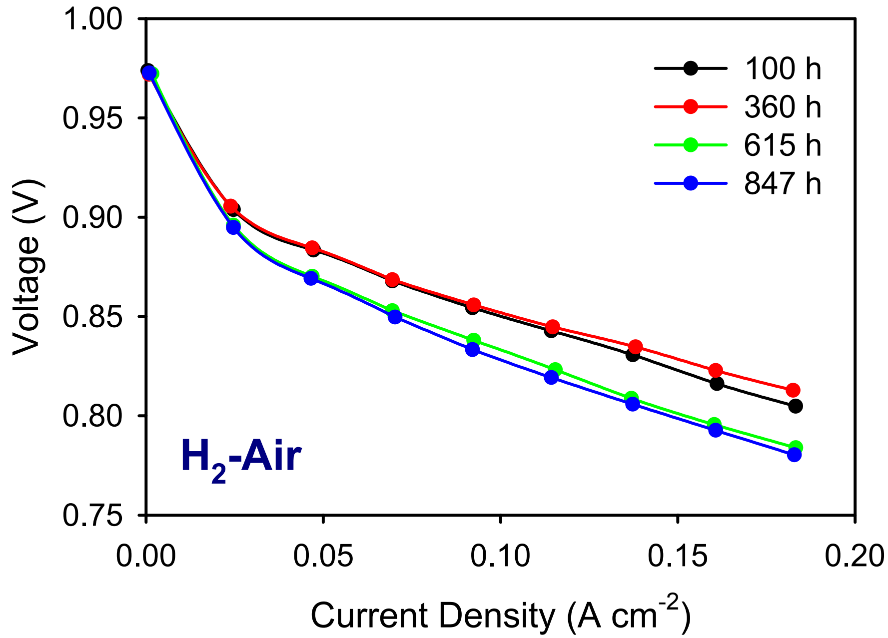


- ***Surface area loss of the cathode and/or anode catalyst***
- ***Cathode surface oxidation***
- ***Diminished cathode hydrophobicity → "flooding"***
- ***Ruthenium crossover and subsequent accumulation at the cathode***

Durability Research

Ruthenium Crossover: Effect on Oxygen Reduction

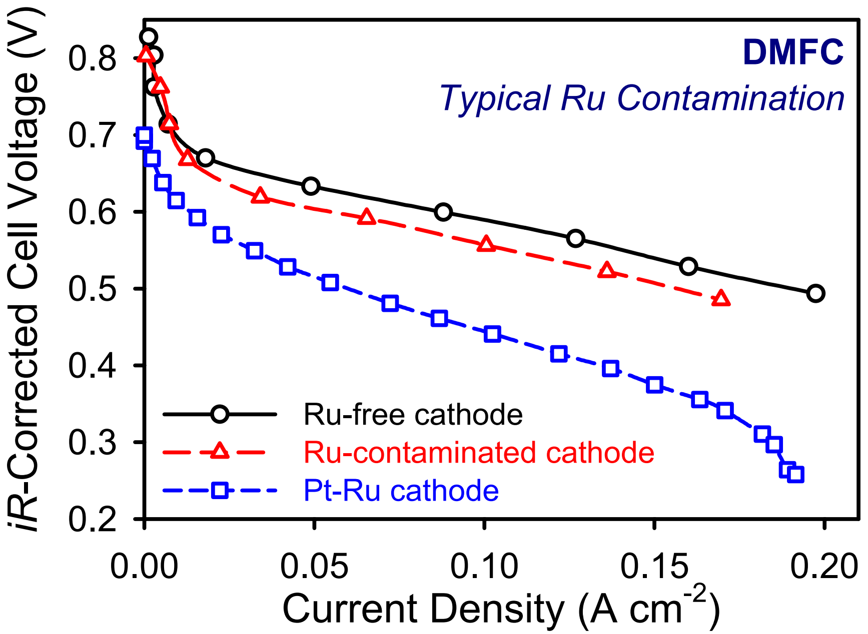


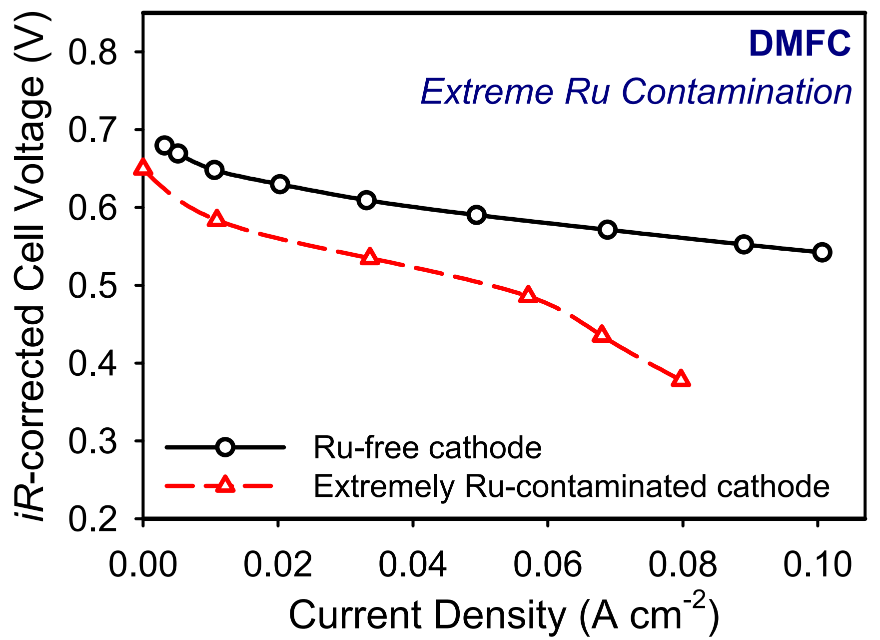


- ***Cathodes in 'typical" DMFCs (Pt-Ru black anode, Nafion™ membrane, Pt black cathode) become gradually contaminated by Ru migrating from the anode.***
- ***CO stripping data at different stages of the life test correlate well with the cathode's kinetic performance.***
- ***Oxygen reduction alone is inhibited by Ru crossover by ~25 mV at 0.1 A cm^{-2} after several hundred hours of cell operation.***

Durability Research

Ruthenium Crossover: DMFC Performance Loss



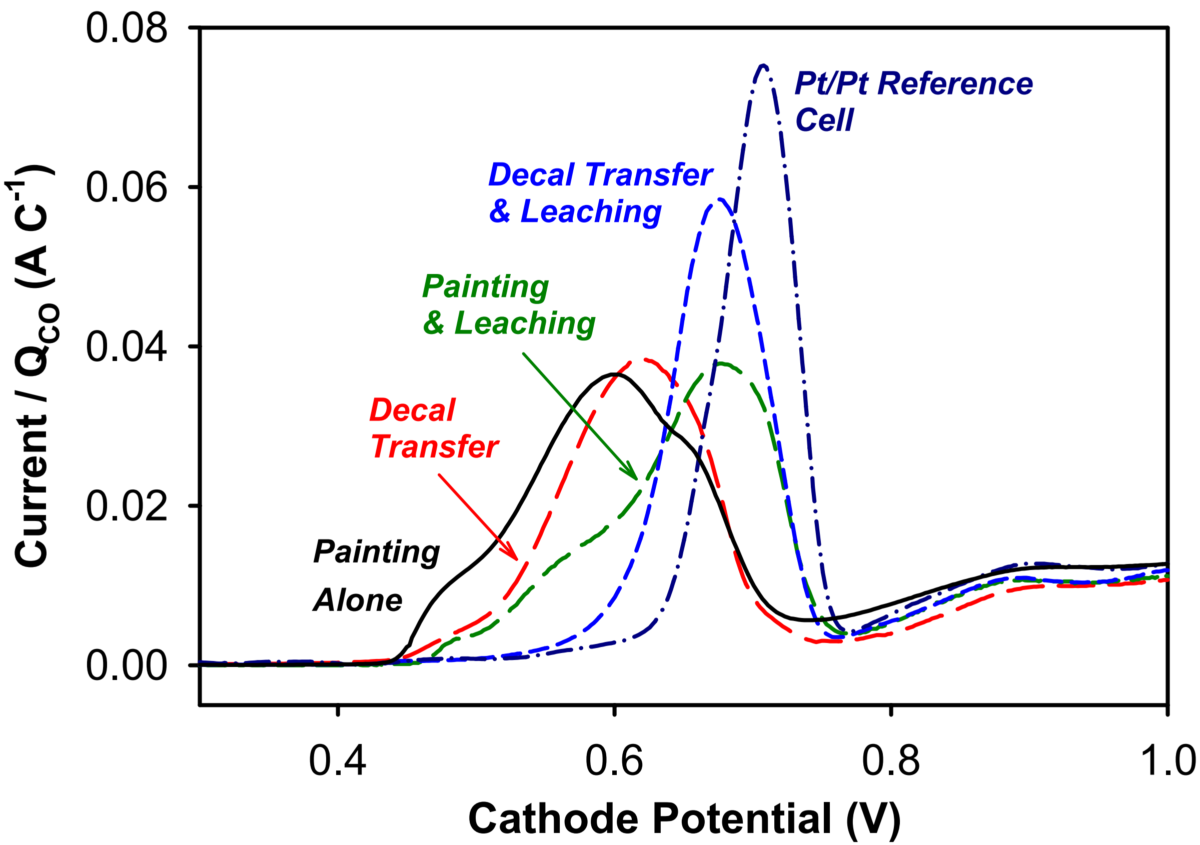


- ***Overall DMFC performance penalty resulting from slower oxygen reduction and lower cathode tolerance to crossover methanol: ~ 40 mV (moderate Ru contamination of the cathode after hundreds of hours of DMFC operation).***
- ***Extreme Ru-contamination: ~ 200 mV cell voltage loss.***

2004 Milestone Accomplished

Durability Research

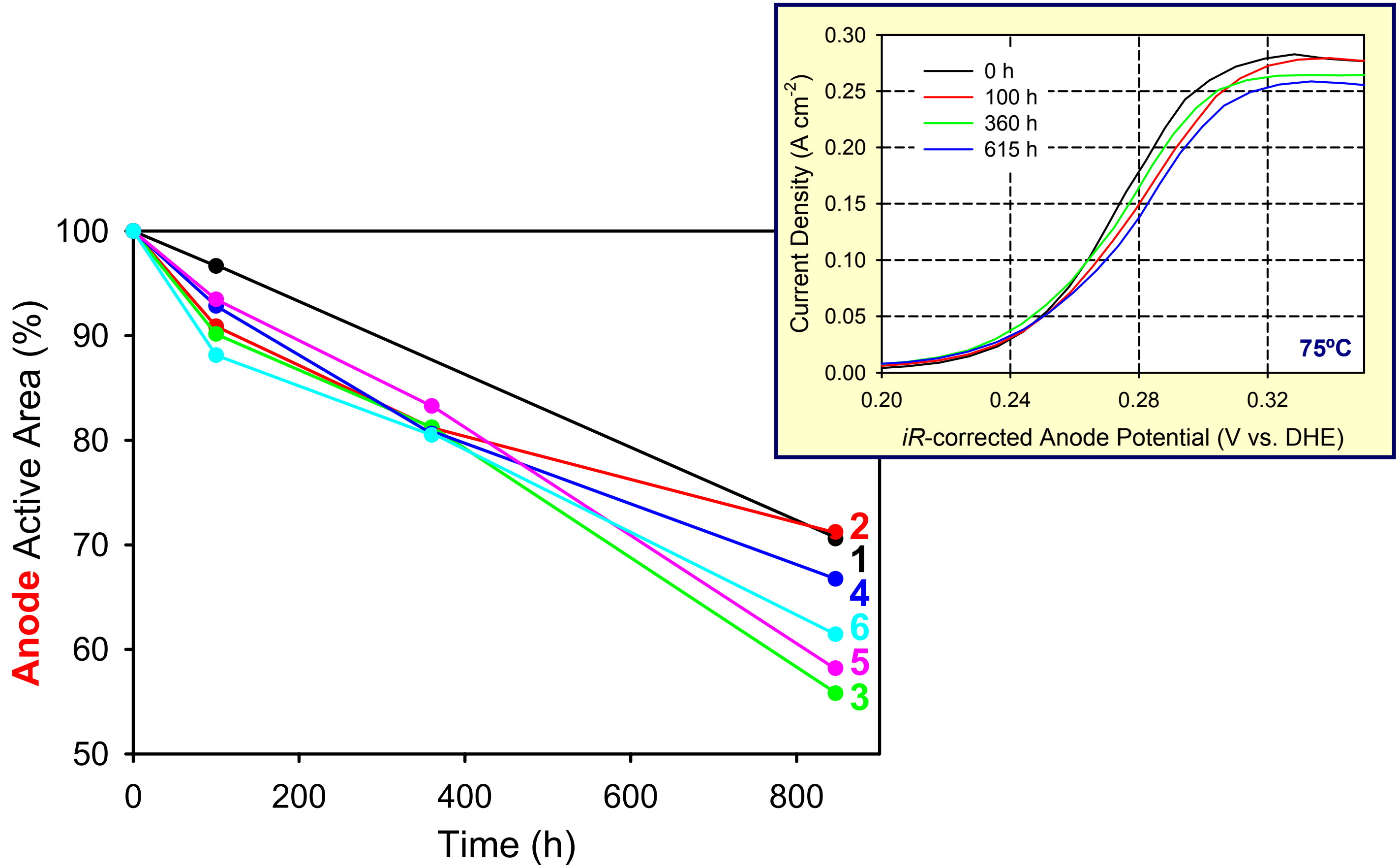
Ruthenium Crossover: Preparation of MEAs with "Ru-free" Cathodes



- ***Virtually Ru-free cathodes observed following removal of loosely-bound Ru in the anode catalyst & better anode curing (after break-in data; no life-tests performed).***

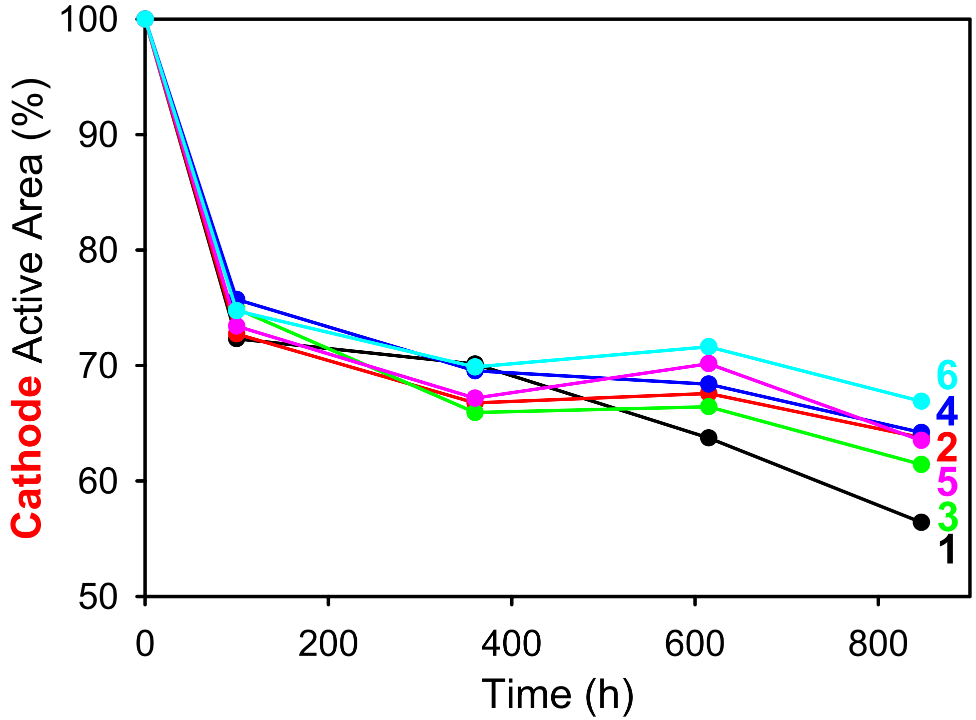
Durability Research

Loss of Anode Active Surface Area



- ***35% - 40%* anode surface area loss revealed by CO stripping after 850 hours of cells operation.**
- ***Very little impact on DMFC performance.***

Durability Research
Loss of Cathode Active Surface Area

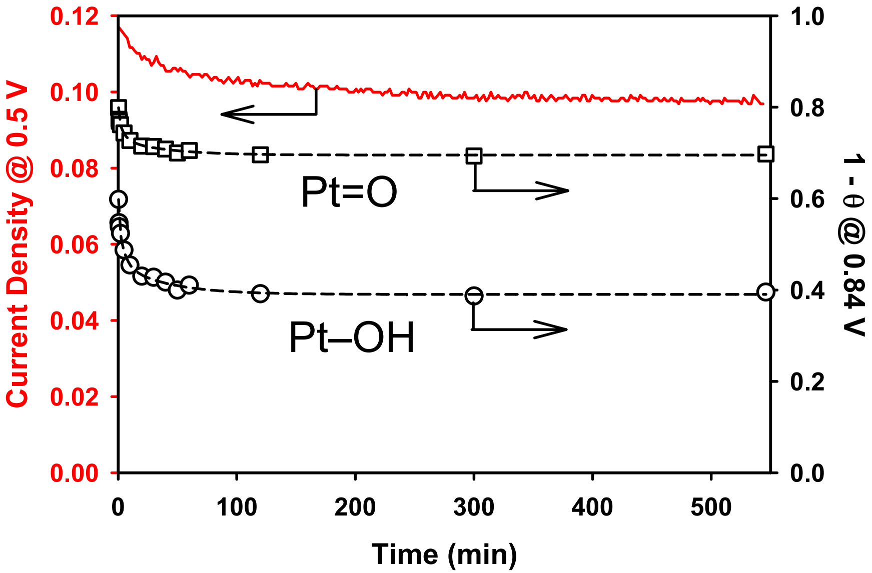


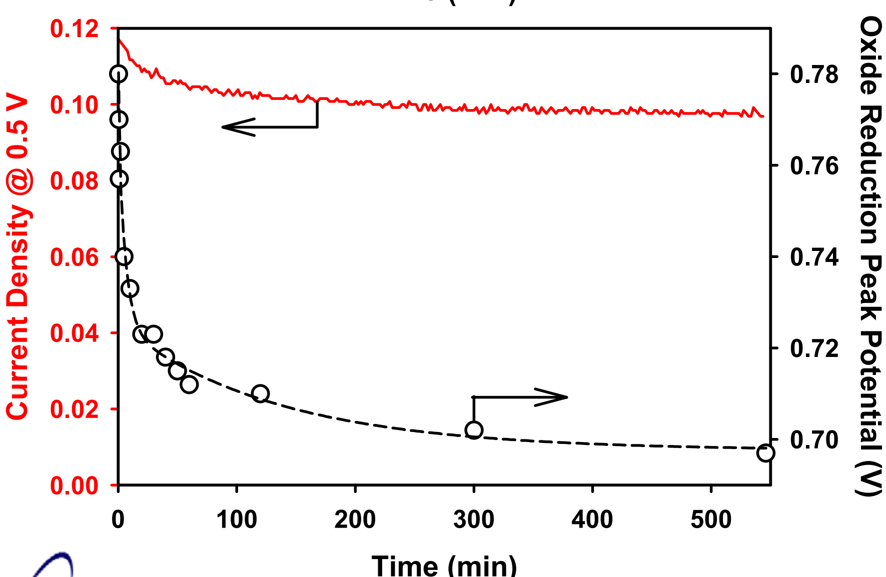
- ***35% - 40% cathode surface area loss revealed by CO stripping after 850 hours of cells operation (similar loss as for the anodes).***
- ***Possible significant impact on cell performance.***

2004 Milestone Accomplished & Exceeded

Durability Research

Cathode Oxidation vs. DMFC Performance Loss



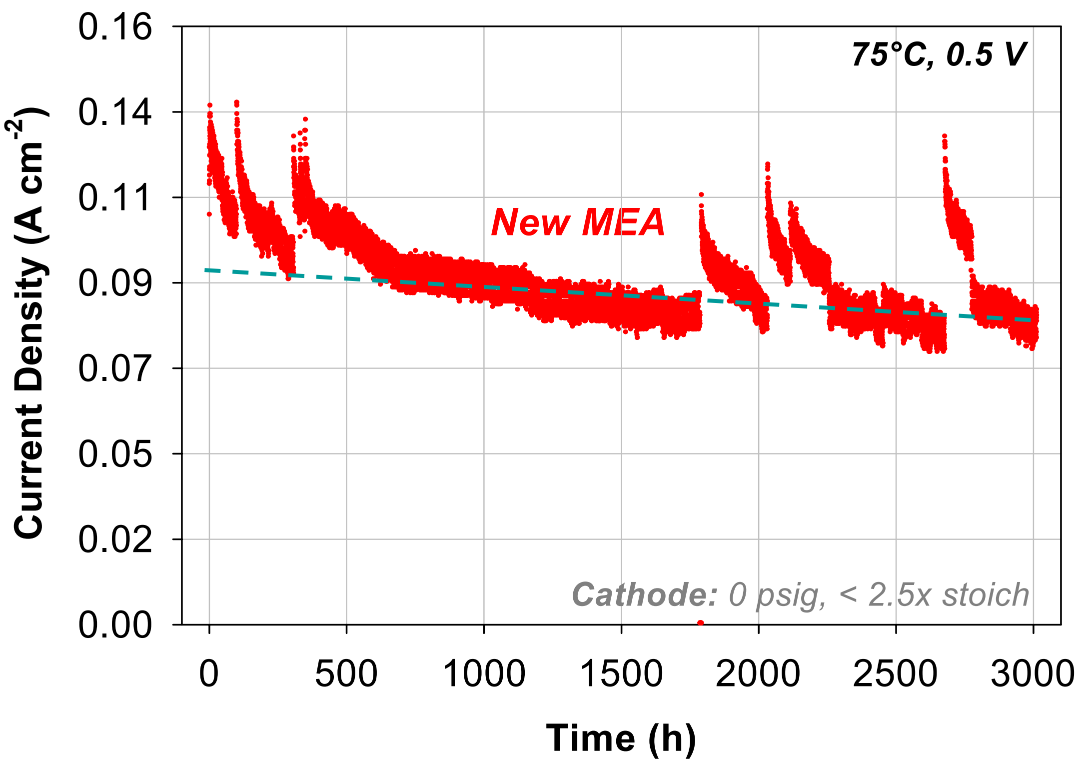


- ***No obvious correlation observed between <u>the rates</u> of catalytic sites blockage by surface 'OH' and/or 'O' species and DMFC performance loss.***
- ***Based on percent loss of cell performance over time, 'O' is the more likely surface species.***

- ***Transition of the cathode oxide beyond the point of surface coverage saturation is a likely reason for cell performance drop at times longer than two hours (→ lessened Pt catalyst activity in oxygen reduction reaction).***

Durability Research

Novel DMFC MEA with Improved Stability



- ***New LANL-developed Nafion-based MEA tested for 3000 hours under challenging conditions of low air "stoich" and ambient cathode pressure.***
- ***3000-hour performance loss limited to ~12% (with fully oxidized cathode).***

Technical Accomplishments & Progress *(Highlights)*

Performance Durability:

- ✓ Determined impact of Ru crossover on DMFC cathode performance (Milestone #1); proposed two methods for Ru crossover reduction
- ✓ Quantified anode & cathode surface area losses in the 850-hour life test (Milestone #3)
- ✓ Correlated transformation of Pt oxide and cathode performance loss
- ✓ Demonstrated new Nafion-based MEA with performance loss reduced to ~12% over 3000 hours

Membrane & MEA Research:

- ✓ Demonstrated much higher than Nafion's selectivity of 6F-CN-35 membrane in operating cell
- ✓ Maintained superior performance of the 6F-CN-35 MEA for 700 hours

Cathode Electrocatalysis:

- ✓ Synthesized in-house Pt and Pt-Co catalysts (unsupported and supported) with significantly reduced average particle size – Milestone #2's 40% particle-size reduction goal achieved; work will focus on performance

High Specific-Power Portable Stack:

- ✓ Designed, built and successfully tested first short six-cell stack

Selected Reviewers' Comments

- R *"Astonishing productivity on all key areas of DMFC"*
- R *"Good balance of theoretical understanding and practical experiments. But why move to higher power?"* Higher power stack effort was abandoned in late FY03. Instead, the project has focused even more on key issues for the future of DMFCs: (i) performance durability, (ii) alternative membrane/MEA development and (iii) cathode operation. Small effort has continued in the high specific-power DMFC stack, the project now internally supported by LANL..
- R *"Transfer stack making technology to an industrial company"* A government-use license has been issued to Ball Aerospace for military applications (20 W portable system). Several companies expressed significant interest in the stack, methanol-sensor and novel-MEA technologies. Substantial discussions in progress.
- R *"Stay with your strengths – focus on improving performance and fundamental understanding"* These have actually been the two main thrust areas of the DMFC research at LANL in FY04.
- R *"Continue funding"*

Research Plans

Remainder of FY 2004

- Determine and optimize performance of new LANL-synthesized highly-dispersed cathode catalysts
- Verify performance stability of novel Nafion-based MEAs, recently life-tested for 3000 hours
- Demonstrate a complete 25-cell high specific-power stack for portable applications

FY 2005 Objectives *(All key to successful commercialization of DMFCs)*

- Determine impact of changing hydrophilic/hydrophobic properties of the cathode on DMFC performance and performance durability
- Explore introduction of non-precious metal electrocatalysts as means of lowering DMFC cost
- Minimize or altogether eliminate Ru crossover in DMFCs
- Establish materials and techniques allowing consistent fabrication of highly selective and durable alternative MEAs for DMFCs

DMFC Research: Project Safety

Administrative Safety Controls

- ✓ ***Hazard Control Plan (HCP):*** *Hazard-based safety review*
- ✓ ***Integrated Work Document (IWD):*** *Task-based safety review*
- ✓ ***Integrated Safety Management (ISM):*** *Define work → Analyze Hazards → Develop controls → Perform work → Ensure performance*

Engineering Controls

- ✓ ***Hydrogen and carbon monoxide laboratory sensors for hydrogen testing (cell break-in, anode polarization testing, surface area determination)***
- ✓ ***In the process of replacing tube hydrogen gas storage with on-demand electrolytic hydrogen generators***
- ✓ ***Generally low and very low risk operations***

Potentially Useful DMFC Safety Tip

- ✓ ***Direct sink disposal of low-concentration aqueous methanol waste is acceptable after dissolved CO_2 is removed by neutral gas purging and, consequently, initially acidic solution pH increases to neutral.***